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Synthesis of new ferrocenyl derivatives and their use in the first cyclopropanation of fullerene C_{60} with ferrocenes

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Abstract

New ferrocenyl derivatives (a β-ketoester and a β-diester) were synthesised and linked to fullerene C_{60}, with the aim to elucidate factors involved in intramolecular electronic communication. These are the first examples of fullerene functionalised with ferrocenes via the cyclopropanation reaction. The resulting dyads were characterised.

Keywords: Cyclopropanation; Ferrocenyl derivatives; Fullerene; Ferrocenes

1. Introduction

Fullerene derivatives are being prepared in an increasing number, because of their interesting applications, e.g. in modified biomolecules and medicinal chemistry [1] or in material science [2]. In particular, electron transfer systems are of interest, since they are related to the problem of artificial photosynthesis [3]. In this respect, the coupling of a strong electron-attracting moiety, as C_{60}, with a strong electron-donating species, as the ferrocenyl group, is promising and a number of dyads and triads containing both Fc (ferrocenyl) and C_{60} moieties have been described [4]0. However, the ferrocenes used for the construction of ferrocene–fullerene dyads were generally commercial compounds. We report here the preparation of new ferrocenyl derivatives, designed ad hoc, in order to obtain substrates suitable for introduction in ferrocene–fullerene dyads. Moreover, these compounds were used to prepare the dyads, applying for the first time the Bingel [5] cyclopropanation with ferrocenes.

2. Results and discussion

Ethyl 3-ferrocenyl-3-oxopropanoate, $FcCOCH_2CO_2Et$, was prepared in a 76% yield from ferrocene and ethyl 2-chlorocarbonylethanoate, by a Friedel–Crafts acylation. The β-ketoester, pure at the gas chromatographic analysis, showed a mass spectrum with $M^+ = 300\ m/z$ (MF, 300.14) and a ^{1}H-NMR spectrum complicated by the presence of some amount of the enol form (enolic OH at δ 17 ppm), but in agreement with what expected for a mono-substituted ferrocene.

Ethyl ferrocenylmethyl propanedioate, $FcCH_2OCOCH_2CO_2Et$, was prepared in a 82% yield from ferrocenylmethanol, $FcCH_2OH$ (that, in turn, was obtained reducing with $NaBH_4$ the commercially available ferrocenecarboxyaldehyde, FcCHO) and ethyl 2-chlorocarbonylethanoate. The obtained β-diester, pure at the GC analysis, presented a mass spectrum with $M^+ = 330\ m/z$ (MF, 330.16) and a ^{1}H-NMR spectrum characteristic of a mono-substituted ferrocene.

Both ferrocenyl derivatives were reacted with fullerene in anhydrous toluene, in the presence of I_2 and DBU (1,8-diazabicyclo[5.4.0]-7-undecene). Reagents, conditions, and yields for all the reactions were reported in Scheme 1. Dyads **1** (MF, 1018.78) and **2** (MF,

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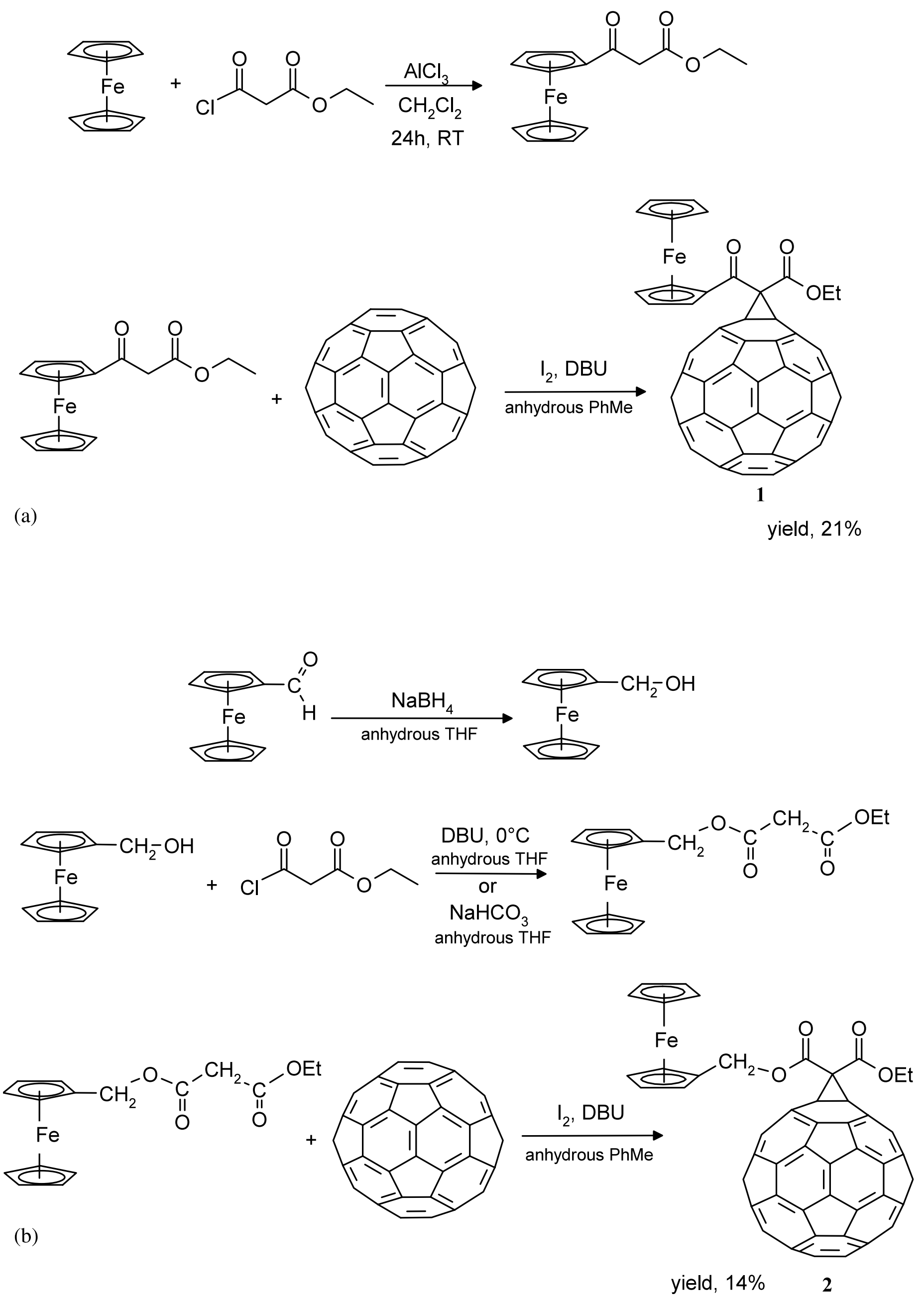


Scheme 1. Synthesis of ferrocene precursors and of ferrocene–fullerene dyads.

1048.79) were purified by column chromatography, with purity checked via HPLC, and characterised by MALDI-TOF mass spectrometry (Fig. 1). Attempts to grow crystals for X-ray analysis failed. ^{1}H-NMR spectra in $CDCl_3$ changed with concentration, probably as a consequence of molecular stacking. Moreover, it was very difficult to get completely rid of toluene from the reaction. The signal of $COCH_2CO$ disappeared in the spectra of both **1** and **2**. The low solubility prevented the possibility to obtain ^{13}C-NMR spectra. IR spectra maintained features typical of fullerene (720 cm^{-1}) and mono-substituted ferrocenes (1001 and 1105 cm^{-1}), [6]beside the CO absorption (1745 cm^{-1}). Significant changes were observed in electronic spectra, both in λ_{max} and in molar extinction, ε, as reported in Table 1. In particular, in the range 280–320 nm a large variation of spectra was observed, as illustrated in Fig. 2, where the spectra of equimolar solutions of $FcCOCH_2CO_2Et$, fullerene, and the dyad **1** are reported.

Voltammetric measurements in anhydrous CH_2Cl_2 evidenced a shift in oxidation potential, from 0.79 V of $FcCOCH_2CO_2Et$ to 0.66 V of dyad **1**. For the latter, two reduction potentials were also recorded, at −0.59 and

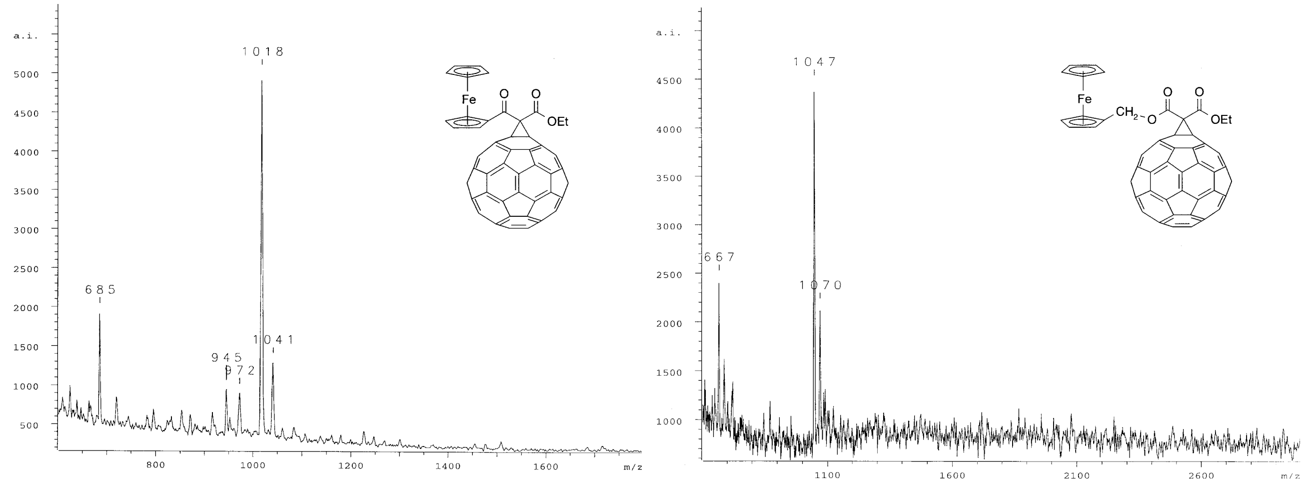


Fig. 1. MALDI-TOF mass spectra of fullerene–ferrocene dyads **1** and **2**.

Table 1
Electronic spectra of dyads **1** and **2**, compared with those of ferrocene precursors and fullerene

Compound	$\lambda_{\max}$	ε	Concentration (M)
Fullerene	329, 406	38100, 2200	6.1×10^{-5}
$FcCOCH_2CO_2Et$	322, 463	2100, 500	3.3×10^{-4}
Dyad **1**	318, 426, 468	31600, 2000, 1700	6.2×10^{-5}
$FcCH_2OCOCH_2CO_2Et$	320 (sh), 454	–, 200	1.5×10^{-3}
Dyad **2**	327, 428, 456	19200, 8300, 11100	2.5×10^{-5}

Solvent, CH_2Cl_2.

−0.95 V, shifted from those of fullerene (−0.44 and −0.82 V, respectively [7]). Although the variations may seem not very large, they are higher than those of other examples in the literature [8].

As to dyad **2**, only preliminary data are available (a reduction potential at −0.61 V and a very weak oxidation potential at 0.39 V). In order to have better data, better work is necessary to optimise the analysis conditions, especially in view of the problems related to the recently discussed retro-Bingel electrochemical reaction [9].

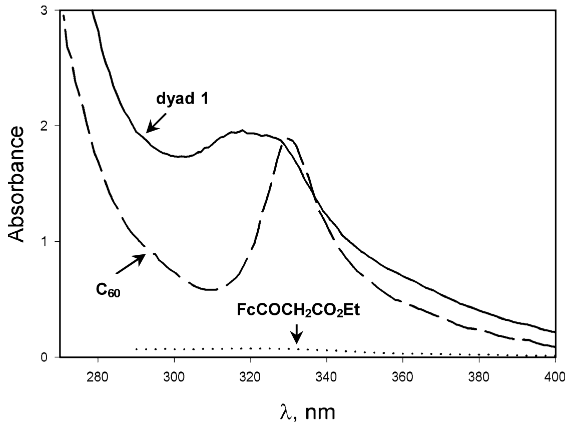


Fig. 2. Comparison of the electronic spectra of ethyl 3-ferrocenyl-3-oxopropanoate (dotted line), fullerene (dashed line), and dyad **1** (solid line) at the same concentration (6.1×10^{-5} M in $CHCl_3$).

These results are indicative of some electronic communication within the molecule and work is in progress to link other β-dicarbonyl derivatives of ferrocene to fullerene, with the aim to fine-tuning the structure in order to obtain better intramolecular electronic transfer.

3. Experimental

Gas chromatographic analyses have been carried out with a Varian CP3000 instrument, equipped with a 30 m × 0.25 mm capillary column (methylsilicone). A Bruker AM400 spectrometer was used to obtain ^1H- and ^{13}C-NMR spectra, as $CDCl_3$ solutions with Me_4Si as the internal standard. Gas–mass spectrometry analyses have been performed with a GC/MS Shimadzu CP6000 system (30 m × 0.25 mm capillary column). Direct inlet (FAB) mass spectra were obtained with a VG Quattro spectrometer. MALDI-MS measurements were performed on a Reflex time-of-flight instrument (Bruker-Franzen Analytik, Bremen, Germany) equipped with an SCOUT ion source, operating in linear positive mode. Ions, formed by a pulsed laser beam (nitrogen laser; $\lambda = 337$ nm), were accelerated to 25 kV. Pulsed ion extraction (PIE) was done applying to the second grid a voltage of 23 kV for 150 ns. 2,5-Dihydroxybenzoic acid (DHB) was used as matrix (10 mg ml^{-1} in acetone). About 0.5 mg of each sample was dissolved in 1 ml of chloroform. 5 μl of sample solution was added to the same volume of matrix solution. 1 μl of the resulting mixture was deposited on the stainless steel sample holder and allowed to dry before introduction into the mass spectrometer. External mass calibration was made using the $[M+H]^+$ ions of DHB (*m*/*z* 155), Angiotensin II (*m*/*z* 1047) and bovine insulin (*m*/*z* 5734).

Infrared spectra were recorded with a Perkin–Elmer IR783 spectrophotometer, in Nujol (NaCl disks). UV measurements were carried out with a Hewlett-Packard 8452A diode array spectrophotometer. HPLC analyses were performed with a Shimadzu LC-10 AD instrument, equipped with a 5 μm MetaPhor ODS-2 column (reverse phase) as an UV–Vis diode array SPD-M10A detector.

Voltammetric measurements were carried out with a Solatron 1285 instrument, equipped with software Corr Ware, electrochemical cell with nitrogen inlet and outlet, and Pt electrodes. The measurements were performed in 0.1 M tetrabutylammonium perchlorate in anhydrous CH_2Cl_2, using SCE as the reference electrode.

3.1. Synthesis of ferrocenes

All the syntheses required dried glassware, dry solvents, and inert atmosphere.

Ethyl 3-ferrocenyl-3-oxopropanoate, $FcCOCH_2CO_2Et$. 5.6 g ferrocene (30 mmol) and 4 ml $ClCOCH_2CO_2Et$ (4.5 g, 30 mmol) in 150 ml CH_2Cl_2 were added dropwise to a suspension of 6.0 g $AlCl_3$ in 70 ml of the same solvent. After 24 h stirring, the solution was poured into 250 ml of aqueous 5% ammonium chloride and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous sodium sulphate, and evaporated. The crude mixture was purified by column chromatography (silica gel, chloroform). The product, eluted as the second fraction, was recrystallised from pentane, to give 6.84 g of a red solid (yield, 76%): m.p., 36–37 °C.

These reaction conditions gave a result better than that from a previous run, performed at the reflux temperature for 10 h. Although the compound from the column chromatography is pure, it is liquid and decomposes, even if stored in the refrigerator. Therefore, the recrystallisation is necessary in order to obtain the ketoester as a solid, that is more stable.

GC/MS: *m*/*z*, 213 $[M^+ - CO_2Et]$, 185 (Fc^+). MS (FAB, 3-nitrobenzyl alcohol): *m*/*z*, 301 $[M^+ + H]$. ^{1}H-NMR ($CDCl_3$) δ 1.21 (t, $J = 6.7$ Hz, 3H, CH_2CH_3), 3.65 (s, 2H, $COCH_2CO$), 4.14 (complex, 7H, superposition of unsubstituted Cp ring and CH_2CH_3), 4.47 (complex, 2H, β-protons of the substituted Cp ring), 4.70 (complex, 2H, α-protons of the substituted Cp ring) ppm. Resonances (δ) of ^{13}C-NMR spectra ($CDCl_3$) are reported in Scheme 2.

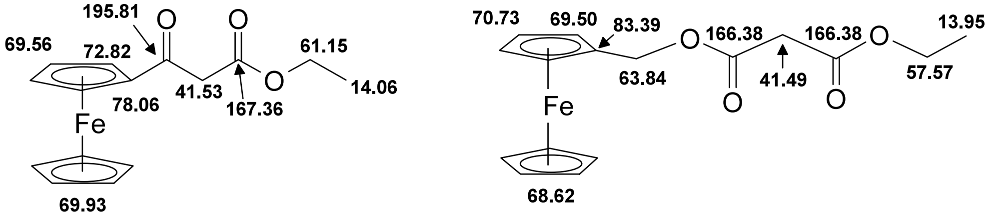
Ethyl ferrocenylmethyl propanedioate, $FcCH_2OCOCH_2CO_2Et$. $FcCH_2OH$ (1.1 g, 5.1 mmol) and $ClCOCH_2CO_2Et$ (0.7 g 5.1 mmol) in 15 ml anhydrous THF was added dropwise to a suspension of $NaHCO_3$ in 20 ml anhydrous THF containing 1 ml 2,2-dimethoxypropane, as a water scavenger. The mixture was stirred 12 h at room temperature, then poured into water and extracted with diethyl ether. By evaporation of the solvent, the diester was obtained as the sole product (GC analysis). Recrystallisation from pentane and cooling afforded 1.38 g of the diester, as a yellow solid that melted out of the refrigerator; yield, 82%.

These reaction conditions gave a result better than that from a previous run, performed with DBU as the base, at 0 °C. 2 mmol $FcCH_2OH$ and 2 mmol DBU in 50 ml anhydrous THF were added dropwise to 3.4 mmol $ClCOCH_2CO_2Et$ in 20 ml anhydrous THF at 0 °C and then reacted 10 h at room temperature, under inert atmosphere. After usual work-up, $FcCH_2OCOCH_2CO_2Et$ (1.4 mmol; yield, 70%) was obtained as the only product.

MS (EI, 70 eV): *m*/*z*, 330 $[M^+]$, 199 ($FcCH_2^+$). MS (FAB, 3-nitrobenzyl alcohol): *m*/*z*, 331 $[M^+ + H]$. IR (Nujol) $\nu_{CO} = 1725, 1745$ cm^{-1}; $\nu_{Cp} = 1002, 1105$ cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.22 (t, $J = 7$ Hz, 3H, CH_2CH_3), 3.35 (s, 2H, $COCH_2CO$), 4.15 (complex, 9H, superposition of unsubstituted Cp ring, β-protons of the substituted Cp ring and CH_2CH_3), 4.25 (complex, 2H, α-protons of the substituted Cp ring), 4.92 (s, 2H, $FcCH_2O$) ppm. Resonances (δ) of ^{13}C-NMR spectra ($CDCl_3$) are reported in Scheme 2.

3.2. Synthesis of dyads

Equivalent amounts (0.1 mmol) of the ferrocenyl derivative, fullerene C_{60}, and iodine in anhydrous toluene were reacted with DBU (0.3 mmol) for 16–18 h, at room temperature, under inert atmosphere. The dyads were purified by column chromatography (silica gel, 1:1 (v/v) toluene–hexane to recover unreacted fullerene, then toluene to elute the dyad). The purity was checked by HPLC (reverse phase column, toluene).



Scheme 2. ^{13}C-NMR chemical shifts of ferrocene derivatives.

Dyad 1, from ethyl 3-ferrocenyl-3-oxopropanoate. MS (MALDI-TOF): *m/z* 1018 [M^+]. IR (Nujol) $\nu_{CO} = 1700, 1745$ cm^{-1}; $\nu_{Cp} = 1002, 1105$ cm^{-1}; $\nu_{C60} = 720$ cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.20 (t, $J = 6.7$ Hz, 3H, CH_2CH_3), 4.35 (s, 2H, CH_2CH_3) partially superimposed with 4.40 (s, 5H, unsubstituted Cp ring), 4.60 (complex, 2H, β-protons of the substituted Cp ring), 4.70 (complex, 2H, α-protons of the substituted Cp ring) ppm.

Dyad 2, from ethyl ferrocenylmethyl propanedioate. MS (MALDI-TOF): *m/z* 1047 [$M^+ + H$]. IR (Nujol), $\nu_{CO} = 1745$ cm^{-1}; $\nu_{C60} = 720$ cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.3 (t, $J = 7$ Hz, 3H, CH_2CH_3), 4.45 (complex, 9H, superposition of unsubstituted Cp ring, β-protons of the substituted Cp ring, and CH_2CH_3), 4.70 (complex, 2H, α-protons of the substituted Cp ring), 5.00 (s, 2H, $FcCH_2O$) ppm.

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